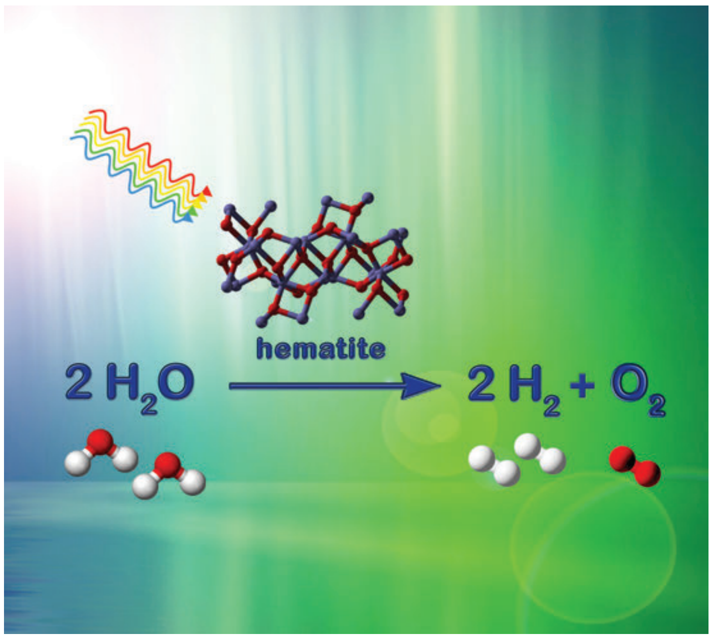
ALS SCIENCE HIGHLIGHT

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Two Electron Holes in Hematite Facilitate Water Splitting

Hydrogen is an attractive form of fuel because its only by-product is nonpolluting water vapor. The problem, however, is that the production of hydrogen—via the process of water splitting—currently requires the burning of traditional fossil fuels. Therefore, water splitting by photoelectrochemical cells (PECs) fueled by solar power has long been a primary goal of sustainable energy research. One roadblock to this goal is that the search for stable, affordable, high-performance PEC electrodes has so far failed to identify an ideal material. Now, researchers from Switzerland, China, and Berkeley have gained an in-depth understanding of the electronic structure of hematite (iron oxide), a promising PEC photoanode candidate, by performing in situ and *operando* soft x-ray spectroscopy at ALS Beamline 7.0.1.



A molecular glance at water splitting. Hematite could play an important role in the generation of hydrogen by solar-powered water splitting, resulting in a truly zero-emission form of energy.

Hematite (α-Fe_2O_3), the mineral form of iron oxide (i.e., rust), is an interesting PEC photoanode material because of its affordability, availability, good stability, and good spectral match to the solar spectrum. It has a relatively small band gap (2.0 eV), giving it the ability to harvest over 16% of standard solar illumination. Although the conduction band of hematite is too low to reduce water, when a dc bias is applied, such as in a tandem cell, water splitting is possible. However, the incident-photon-to-current efficiency (external quantum efficiency) of hematite is less than that of other metal oxides due to its electronic structure, which causes an ultrashort electron–hole excited-state lifetime. Because of inefficient charge separation, the photocurrent produced is limited by the holes that reach the semiconductor–liquid junction. Recent efforts to optimize the nanostructured morphologies of hematite photoanodes have led to significant improvements in performance, but in spite of these efforts, the overall solar-photon-to-photocurrent efficiency in hematite remains at only about a third of its potential.

Thus, a complete understanding of the surface electronic states of hematite has so far been the subject of much interest as well as debate. It has historically been suspected that in hematite, two different holes are formed with different water-splitting power. The existence of different types of holes with disparate reactivity toward water oxidation has broad implications for the ultimate performance of hematite.

Publication about this research: A. Braun, K. Sivula, D.K. Bora, J. Zhu, L. Zhang, M. Grätzel, J. Guo, and E.C. Constable, "Direct observation of two electron holes in a hematite photo-anode during photoelectrochemical water splitting," *J. Phys. Chem. C* **116**, 16870 (2012).

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Research funding: Hydrogen Program of the Swiss Federal Office of Energy, the Swiss National Science Foundation, and the European Community. Operation of the ALS is supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

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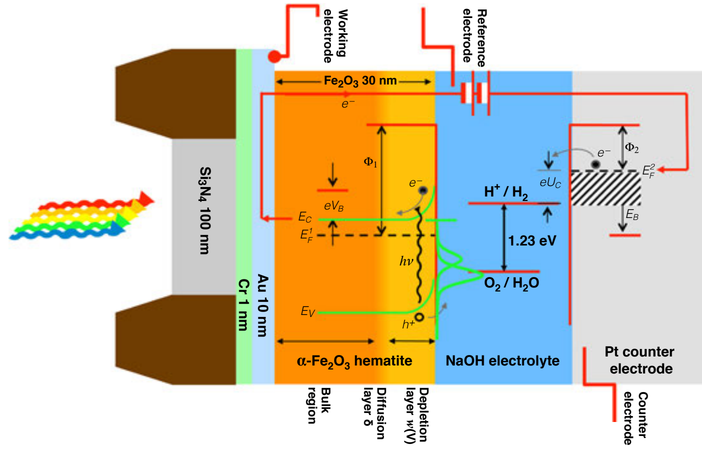
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But studies of this phenomenon are complicated by the fact that the holes needed for solar-powered water splitting by hematite require an anodic electric bias in addition to

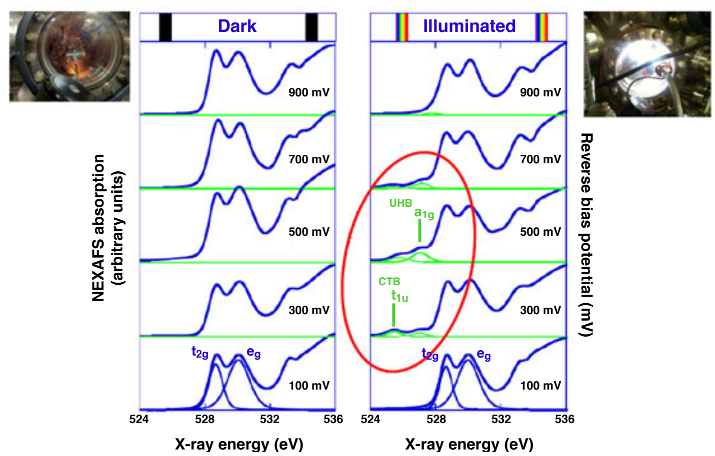
Helpful Holes in Hematite

Electrons are well-known charge carriers, indispensable in our daily lives, but they do not play this role alone. When an electron leaves its assigned place, it leaves behind a hole that can effectively behave like a positive charge carrier, provided that the electron and hole remain separated and do not recombine. In modern semiconductor electronics, holes are important charge carriers without which devices like batteries, capacitors, fuel cells, solar cells, and photoelectrochemical cells (PECs) could not operate. PEC electrodes typically form electron–hole pairs when struck by sunlight. In PEC photoanodes made of hematite, the generated holes must diffuse to the surface, where they can oxidize water to form oxygen. However, the electronic structure of hematite is such that the photogenerated holes tend recombine with the electrons before reaching the surface.

In this work, Braun et al. studied the nature of photoelectrically generated holes in a PEC specially designed for gathering data while the cell is in operation ("*operando*"). The results demonstrated the formation of two different types of electron holes at the semiconductor–liquid junction under the exact conditions at which a photocurrent arises. Quantitative analysis of their spectral signatures revealed that both types of holes, contrary to earlier speculation and historical perception, contribute to the photocurrent. This is a milestone in our understanding of solar water splitting and encouraging news for researchers worldwide who are working to optimize hematite for PEC photoanodes.



Schematic of the photoelectrochemical cell assembly showing the electrolyte (blue) in contact with the hematite (orange) and a platinum counter electrode (gray). Holes (h^+) are created in the hematite when electrons (e^-) near the surface are excited by simulated sunlight. Overlaid in green are the energy band positions for the conduction band (E_C) and Fermi energy (E_V) as well as spectroscopic curves representing two types of holes. Also shown are the relevant energy positions for the flat band and oxygen and hydrogen evolution according to the theory of Schottky, Marcus, and Gerischer [Bak et al., *Int. J. Hydrogen Energy* 27, 991 (2002)].



Oxygen 1s NEXAFS spectra obtained from the hematite film while in contact with the electrolyte under a bias potential from 100 to 900 mV in dark (left) and illuminated (right) conditions. At 300 mV and under illumination, new spectral features appear at around 525 eV (UHB = upper Hubbard band; CTB = charge-transfer band). The fact that these transitions only appear under bias and illumination leads to the conclusion that they originate from the same electron hole transitions that cause the photocurrent.

optical illumination. Moreover, the holes are transitional and quite elusive.

In this work, the researchers used a specially designed soft x-ray in-situ/*operando* cell developed at the ALS to perform photoelectrochemical experiments with state-of-the-art silicon-doped and nanostructured hematite photoanodes in alkaline electrolyte. They recorded near-edge x-ray absorption fine-structure (NEXAFS) spectra under simulated sunlight and in the dark. Under these conditions, two new spectral signatures evolved in the valence band, which the researchers identified as an O 2*p* hole transition into the charge-transfer band and an Fe 3*d*-type hole transition into the upper Hubbard band.

This is the first time that an analysis of the electronic structure of a PEC photoanode has been performed *operando* under control of an electrochemical potential. Two different hole transitions were identified, validating a long-speculated electronic aspect of hematite. The O 2*p* hole appears and disappears at a potential below that of the Fe 3*d* hole, suggesting that it is more reactive at the same potential. In contrast to established perception, the Fe 3*d* hole, less energetic than the O 2*p* hole but with a larger spectral weight, is also active for water activation, and there is little difference in their activity.